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**Effect of Trichlorofluoromethane  
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Solar Radiation**

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# EFFECT OF TRICHLOROFLUOROMETHANE AND MOLECULAR CHLORINE ON OZONE FORMATION BY SIMULATED SOLAR RADIATION

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## SUMMARY

In this work, mixtures of air with either molecular chlorine ( $\text{Cl}_2$ ) or trichlorofluoromethane ( $\text{CFCl}_3$ ) were photolyzed in a reaction chamber by simulated solar radiation. The purpose was to study the effect of these additions on ozone ( $\text{O}_3$ ) formation in air. One or two parts per million (ppm) of  $\text{Cl}_2$  temporarily inhibited  $\text{O}_3$  formation. However, the  $\text{O}_3$  concentration eventually rose almost to the level for pure air. In the presence of  $\text{CFCl}_3$ ,  $\text{O}_3$  formation was permanently inhibited after an initial rise. Depending on  $\text{CFCl}_3$  concentration,  $\text{O}_3$  concentration either leveled off below the steady-state value for pure air or decreased toward zero after reaching a maximum value.

A mechanism consisting of gas-phase and heterogeneous wall reactions is proposed to explain our results. The two wall reactions proposed are the destruction of  $\text{O}_3$  and chlorine (Cl) atoms. The destruction of Cl atoms at the wall is much more important for the  $\text{Cl}_2$ -air mixtures than for the  $\text{CFCl}_3$ -air mixtures. To explain this fact, it is hypothesized that  $\text{CFCl}_3$  molecules are adsorbed on the Teflon surface and poison it for the heterogeneous Cl destruction reaction.

The gas-phase  $\text{CFCl}_3$ -air reaction mechanism, without wall reactions, was also used to calculate  $\text{O}_3$  formation in a stratospheric mixture of 3 parts per billion (ppb) of  $\text{CFCl}_3$  in air. Results showed a significant reduction in  $\text{O}_3$ , compared with pure air at the same stratospheric conditions. This computation does not prove that  $\text{CFCl}_3$  destroys  $\text{O}_3$  in the stratosphere. It does demonstrate that the chemical model for these chamber experiments shows a similar destructive effect on  $\text{O}_3$  when applied at stratospheric conditions.

## INTRODUCTION

Considerable concern has been expressed recently about the destructive effect of chlorofluoromethanes (CFM's) on the ozone ( $\text{O}_3$ ) layer of the stratosphere (refs. 1 to 4). These compounds are released into the atmosphere by man's activity on Earth. Their

chemical inertness allows them to ultimately diffuse into the stratosphere, where they can be photolyzed by the strong ultraviolet radiation present. Chlorine atoms thus formed are hypothesized to participate in the following ozone-destroying chain reaction:



A comprehensive discussion of the entire problem of CFM's in the environment is given by Rowland and Molina (ref. 5).

The exact amount of  $\text{O}_3$  depletion caused by injection of these compounds is still not known. More information must be obtained about the magnitude of other natural sources of Cl atoms and sinks for CFM's that may be present. In addition, the chemistry involved in this theory has not been fully studied. The photolysis of  $\text{CFCl}_3$  was studied by Marsh and Heicklen (ref. 6). A recent laboratory study (ref. 7) has shown that the two most commonly used compounds,  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$ , are dissociated into chlorine atoms by ultraviolet light. However, to the authors' knowledge the effect of these compounds on ozone formation has not been studied in the laboratory. Moreover, the chlorine-oxygen ( $\text{ClO}_x$ ) chemical system must be better understood in the laboratory before predictions of atmospheric effects can be considered really quantitative. This point is made in one of the two reports prepared recently by committees of the National Academy of Science. These reports have surveyed the complete problem of chlorofluoromethane atmospheric effects and are summarized in reference 8. The first report, by the Committee on Impacts of Stratospheric Change, states that these compounds will cause ozone depletion and other serious climatic changes and that their use should be curtailed within 2 years. Additional work is needed to compute more accurately the predicted ozone depletion within this 2-year period. The second report, by the Panel on Atmospheric Chemistry, gives the current state of knowledge of the ozone threat. It states that the complete chemical model for chlorofluoromethane-ozone interaction still is not known accurately enough to predict quantitatively the ozone depletion by these compounds. In addition, atmospheric measurements of the species involved must be improved.

The authors have completed and reported a laboratory study of ozone depletion by nitric oxide (ref. 9). As a followup to this work, we have started a study of the effects of  $\text{CFCl}_3$  and also molecular chlorine ( $\text{Cl}_2$ ) on ozone formation in air. The purpose of the work is to obtain a better understanding of the  $\text{ClO}_x$  chemical mechanism. For this reason we studied the simpler  $\text{Cl}_2$ -air system first and then went to the more complicated  $\text{CFCl}_3$ -air system. The experimental approach was to irradiate mixtures of several parts per million of either compound with air in a reaction chamber using an ultraviolet light source and to measure ozone concentration as a function of time. All experiments were performed at 1 atmosphere pressure and room temperature (298 K).

A theoretical analysis of our results was performed with the aid of the Lewis Research Center general chemical kinetics computer code (ref. 10).

In this work, quantities of the pollutant used are much larger than quantities present in the stratosphere. This was necessary so that the reactions would proceed to completion in a reasonable laboratory time. Although these laboratory conditions are different from stratospheric conditions, the basic gas-phase chemistry is the same for both situations. Our purpose was to find out whether or not the proposed  $\text{ClO}_x$  system destruction of ozone occurs in a laboratory experiment. This study was intended to give some new information about the complex processes that occur in a reaction chamber.

## APPARATUS AND PROCEDURE

A 650-liter stainless steel chamber was the reaction vessel for this study. This chamber was used previously to study the effect of oxides of nitrogen ( $\text{NO}_x$ ) pollutants on  $\text{O}_3$  formation (ref. 9). For the present investigation, most of the inner walls were covered with Teflon sheets in order to reduce surface reactions involving  $\text{O}_3$  and other active free radicals. The solar simulator was a high-pressure 4.2-kilowatt xenon arc lamp, which provides ultraviolet radiation at wavelengths as low as 200 nanometers. Commercially available tanked gases were used. The clean, dry air used was commercially available ultrapure air. Both  $\text{CFCl}_3$  (99.9-percent minimum purity) and  $\text{Cl}_2$  (99.9-percent minimum purity) were fractionally distilled twice before being used.

The experimental procedure was to obtain time-concentration profiles of  $\text{O}_3$  production in various air mixtures. Both clean, dry air alone and air plus various amounts of pollutant gases, such as  $\text{Cl}_2$  or  $\text{CFCl}_3$ , were irradiated in the reaction chamber at 1 atmosphere and room temperature. As in the preceding paper (ref. 9), these results, when combined with kinetic computer program analyses, could yield useful information on the chemistry of  $\text{O}_3$  and various pollutants.

## EXPERIMENTAL RESULTS

### Chlorine-Air System

Figure 1(a) shows results obtained when air plus various amounts of  $\text{Cl}_2$  were irradiated in the reaction chamber at 1 atmosphere and room temperature. Ozone concentration in parts per hundred million (pphm) is plotted against irradiation time in minutes. Molecular chlorine concentrations were determined by partial pressure measurement techniques. Figure 1(b) shows an expanded portion of figure 1(a) during the first 35 minutes. For comparison, an average of  $\text{O}_3$  formation curves for pure air, ob-

tained just before and after completion of the three  $\text{Cl}_2$ -air runs, is shown as the dashed curve in both figures. These curves show that the presence of  $\text{Cl}_2$  retarded  $\text{O}_3$  formation, and the effect increased as  $\text{Cl}_2$  concentration increased. For 0.8 ppm of  $\text{Cl}_2$ , Cl atom production from  $\text{Cl}_2$  photolysis during the first 2 minutes was insufficient to significantly affect  $\text{O}_3$  formation (fig. 1(b)). After this,  $\text{O}_3$  production was retarded. In the presence of 2.0 and 3.6 ppm of  $\text{Cl}_2$ , Cl atom production after about 1 minute was sufficient to severely retard  $\text{O}_3$  formation for about the next 20 to 30 minutes. In figure 1(a), at the 250th minute,  $\text{O}_3$  concentration for all three  $\text{Cl}_2$ -air mixtures approaches that for pure air alone. The fact that at this time the steady-state  $\text{O}_3$  concentration for the 3.6-ppm- $\text{Cl}_2$  - air mixture is very close to that for the 0.8-ppm- $\text{Cl}_2$  - air mixture suggests the existence of an efficient sink for Cl atoms in the chamber. This sink could be attributed to wall reactions (refs. 11 and 12).

### Trichlorofluoromethane-Air System

Figure 2(a) shows some results for  $\text{O}_3$  formation when air containing 1 and 2 ppm of  $\text{CFCl}_3$  was irradiated. Ozone concentration in pphm is again plotted against irradiation time. Ozone production for clean, dry air - a reference  $\text{O}_3$  curve, obtained just before these two runs - is presented. The presence of 1 or 2 ppm of  $\text{CFCl}_3$  affected  $\text{O}_3$  formation. For these  $\text{CFCl}_3$  additions, there was very little change in  $\text{O}_3$  production during the first 10 minutes. This can be compared with the retarding of  $\text{O}_3$  formation shown in figure 1 for  $\text{Cl}_2$  addition. The initial difference in  $\text{O}_3$  formation for  $\text{Cl}_2$  and  $\text{CFCl}_3$  additions can be explained qualitatively by the fact that  $\text{CFCl}_3$  is much more difficult to photolyze.

At times beyond 10 minutes,  $\text{CFCl}_3$  addition retarded  $\text{O}_3$  formation; this effect was observed even up to the 240th minute. This relatively long-term effect for  $\text{CFCl}_3$  was not observed for  $\text{Cl}_2$ . This is somewhat surprising if the retarding effect for both pollutants is due mainly to Cl atoms. A possible explanation can be made in terms of the wall sink for Cl atoms, which was said to be rather efficient for the  $\text{Cl}_2$ -air mixtures. If this sink is less important for  $\text{CFCl}_3$ , more Cl atoms will remain in the gas phase for long-term destruction of  $\text{O}_3$ . Wall destruction of Cl atoms is discussed further in the following section.

Figure 2(b) presents results for further additions of  $\text{CFCl}_3$ . These data were obtained at a much later time than those shown in figure 2(a). The data for 1 and 2 ppm of  $\text{CFCl}_3$  were normalized on the basis of the pure-air reference curve and are shown plotted as a long-dashed curve. As additional  $\text{CFCl}_3$  was added,  $\text{O}_3$  formation was increasingly affected. When 29 ppm or more of  $\text{CFCl}_3$  were initially present,  $\text{O}_3$  formation was drastically reduced after 20 to 40 minutes and never recovered.



## COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

Chemical modeling computations were performed for both chemical systems studied in this work. This was done in an effort to explain our results and to obtain a better understanding of the complex chemical mechanism involved.

### Chlorine-Air System

The important reactions proposed by kineticists for the  $\text{Cl}_2$ -air system are given in table I. The rate constants used for these reactions are also given. The reaction mechanism used to compute  $\text{O}_3$  profiles for our  $\text{Cl}_2$ -air photolysis experiments consists of the reactions in table I plus two additional wall destruction reactions. The first is the extra destruction reaction for  $\text{O}_3$ , namely,  $\text{O}_3 \xrightarrow{k_D} (3/2)\text{O}_2$ . This reaction was needed in our preceding work (ref. 9) to calibrate the chamber for  $\text{O}_3$  wall destruction. In this way, we could compute the observed  $\text{O}_3$ -against-time profiles for pure-air irradiation. The rate constants for this reaction ( $k_D$ ) and also for the  $\text{O}_2$  photolysis ( $J_7$ ) were deduced by computer matching of the  $\text{O}_3$  formation curves for pure air. The values found for the pure-air curve of figure 3 were  $k_D = 4.8 \times 10^{-4} \text{ sec}^{-1}$  and  $J_7 = 2.8 \times 10^{-9} \text{ sec}^{-1}$  for reaction VII.

A wall destruction reaction for chlorine atoms was also needed in the reaction mechanism. As mentioned earlier, the experimental results indicate that a sink for Cl atoms exists in the chamber during the chlorine-air photolysis. Unfortunately, we do not have any experimental measurements to use in calibrating the chamber for Cl atom wall destruction. However, destruction of Cl atoms on a surface is known to occur (refs. 11 and 12). A few computations without a chlorine destruction reaction were quite unsuccessful in reproducing the observed  $\text{O}_3$  profiles. The final computations were made using the first-order Cl removal reaction  $\text{Cl} \xrightarrow{k_{\text{Cl}}} \text{N}_2$  with  $k_{\text{Cl}} = 40 \text{ sec}^{-1}$ . The value of  $k_{\text{Cl}}$  for this simulated surface reaction was determined by several trial computations. The use of this unbalanced reaction does not affect the mass balance of the mixture because the concentration of Cl atoms is always extremely low and the  $\text{N}_2$  concentration is very high.

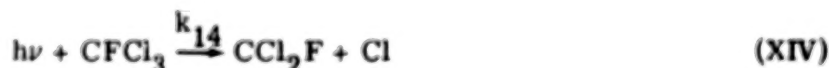
The computed and experimental results are compared in figure 3. The experimental (solid line) curves include the pure-air reference curve. The agreement between experimental and computed (dashed line) curves is quite good. Therefore, the assumed mechanism explains the destruction of  $\text{O}_3$  in the reaction chamber experiments. Analysis of several computational trials shows that the  $\text{O}_3$  formation delay can be explained by three important reactions. The chlorine atoms are generated by the  $\text{Cl}_2$  photolysis, reaction III, which starts the chain mechanism of reactions I and II. Ozone formation

delay is due to  $\text{Cl} + \text{O}_3$ , reaction I. Eventually, the effect of the  $\text{O} + \text{O}_2 + \text{M}$  formation reaction for  $\text{O}_3$  overcomes its destruction by  $\text{Cl} + \text{O}_3$ . When this occurs, ozone concentration then rises as indicated. Although the reactions involving  $\text{ClO}_2$  are of lesser importance, they must be used to explain our results quantitatively.

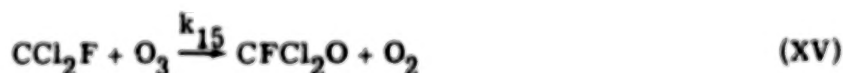
### Trichlorofluoromethane-Air System

A comparison of computed and experimental  $\text{O}_3$  profiles for the irradiation of several  $\text{CFCl}_3$ -air mixtures is shown in figure 4. For these computations the  $\text{Cl}_2$ -air mechanism was used together with new reactions involving the photolysis of  $\text{CFCl}_3$ . The pure-air reference curve in figure 4(a) differs slightly from the ones in figures 4(b) and (c). Both differ from the reference curve used in figure 3, suggesting that the wall characteristics have changed slightly. Therefore, the value of the  $\text{O}_2$  photolysis rate constant was adjusted in figure 4. The values used are  $J_7 = 1.5 \times 10^{-9} \text{ sec}^{-1}$ , for figure 4(a) and  $J_7 = 2 \times 10^{-9} \text{ sec}^{-1}$  for figures 4(b) and (c).

The  $\text{CFCl}_3$  reactions used include, first of all, the photolysis step



According to reference 7 this is the decomposition that occurs above a wavelength of 200 nanometers. The value of  $k_{14}$  used is  $1.3 \times 10^{-6} \text{ sec}^{-1}$  and is in the range of high-altitude values given in reference 3. Information was not available for the direct computation of photochemical rate constants. Therefore, computations were performed for a range of high-altitude values. The chosen  $k_{14}$  gave, in the authors' judgment, the best agreement with experiment, considering both the general shape of the curve and closeness of fit. Three additional reactions involving photolysis fragments from  $\text{CFCl}_3$  were also used. The recent work of reference 13 suggests the reactions



No rate constants are given for these reactions in reference 13, so the values used are estimates. The rate constants  $k_{15}$ ,  $k_{16}$ , and  $k_{17}$  were varied over a wide range of



values with no significant change in the computed results. The computations shown in figure 4 were performed with  $k_{15} = 5 \times 10^{12} \text{ cm}^3/\text{mole sec}$ ,  $k_{16} = 1 \times 10^8 \text{ cm}^3/\text{mole sec}$ , and  $k_{17} = 1 \times 10^{-2} \text{ sec}^{-1}$ . The effect of completely omitting these reactions will be discussed later in this section.

As we have pointed out, our experimental results suggested that the sink for Cl atoms is much less important for  $\text{CFCl}_3$ -air mixtures than for  $\text{Cl}_2$ -air mixtures. Our first computations indicated this also. Moreover, they showed that using a single value of  $k_{\text{Cl}}$  gave poor agreement between computed and experimental results. Better agreement could be obtained when the removal of Cl atoms was decreased as  $\text{CFCl}_3$  concentration was increased. This trend can be justified qualitatively by assuming that  $\text{CFCl}_3$  is adsorbed on the walls of the chamber and poisons the surface for wall destruction of Cl atoms. This kind of effect is discussed by Laidler (ref. 14). Therefore, in the calculations shown in figure 4,  $k_{\text{Cl}}$  was empirically varied to permit a better match with the experimental data. In addition, there might also be some poisoning of the ozone wall destruction reaction, causing a decrease in the value of  $k_{\text{D}}$ . However, Laidler also points out that a gas may be selectively adsorbed on active sites for one reaction and adsorbed very little on the sites for a second reaction. This would be especially true for a porous surface like Teflon. Because  $\text{O}_3$  is relatively much more stable than Cl (especially on a Teflon surface), we have assumed that  $k_{\text{D}}$  is affected much less than  $k_{\text{Cl}}$  by  $\text{CFCl}_3$  adsorption. To obtain the most satisfactory agreement between experiment and computation, the values listed in the following table were used for  $k_{\text{Cl}}$  and  $k_{\text{D}}$ :

Initial $\text{CFCl}_3$ concentration, ppm	$k_{\text{Cl}}$ , $\text{sec}^{-1}$	$k_{\text{D}}$ , $\text{sec}^{-1}$
1	6.0	$3.5 \times 10^{-4}$
2	5.3	$3.0 \times 10^{-4}$
6	4.0	$3.0 \times 10^{-4}$
13	2.8	$3.0 \times 10^{-4}$
29	2.5	$2.0 \times 10^{-4}$
54	2.5	$2.0 \times 10^{-4}$
103	2.5	$2.0 \times 10^{-4}$

Figure 4(a) shows computed and experimental  $\text{O}_3$ -against-time profiles for initial  $\text{CFCl}_3$  concentrations of 1 and 2 ppm. Profiles for initial concentrations of 6 and 13 ppm are shown in figure 4(b); and those for initial concentrations of 29, 54, and 103 ppm are shown in figure 4(c). There is fairly good agreement between experimental and computed curves for 1 and 2 ppm of  $\text{CFCl}_3$ . The computed curves reach their peak values more rapidly than the experimental ones but then level off at about the same steady-

state values as the experimental curves. The agreement for the 29- to 103-ppm  $\text{CFCl}_3$  curves is fair (fig. 4(c)). The computed  $\text{O}_3$  peak heights are good, but the  $\text{O}_3$  concentration falls off too rapidly. The computed concentration then levels off, whereas the experimental  $\text{O}_3$  concentration decreases steadily. There is only semiquantitative agreement between the experimental and computed curves for 6 and 13 ppm of  $\text{CFCl}_3$  (fig. 4(b)).

As stated previously, the actual mechanism of the photodecomposition of  $\text{CFCl}_3$  is not known. We have used three hypothesized reactions (XV to XVII) in addition to the known initial step, reaction XIV. To determine the importance of reactions XV to XVII, ozone profiles were computed with these three reactions removed from the mechanism. The results are shown in figure 5. The solid curves are the computed  $\text{O}_3$ -against-time profiles of figure 4 for the three  $\text{CFCl}_3$  concentrations. The dashed curves are  $\text{O}_3$  profiles computed without reactions XV to XVII. The results are only slightly different. This shows that the fragment reactions are not important in our particular system. The reason for this is probably the fact that a very small percentage of the initial  $\text{CFCl}_3$  is photolyzed in any single experiment. These reactions might be more important under stratospheric conditions of lower pressure and very much smaller  $\text{CFCl}_3$  concentrations. Figure 5 shows that the difference between the solid and dashed curves increases as the initial  $\text{CFCl}_3$  concentration decreases. However, the curves retain the same shape.

## DISCUSSION OF WALL REACTIONS

One reason for the discrepancies between our experimental and computed results is that we have only been able to approximate the complicated wall reaction processes that undoubtedly occur. This is done by assuming that  $\text{CFCl}_3$  is adsorbed on a Teflon surface. The amount of  $\text{CFCl}_3$  on the surface affects the destruction of Cl atoms by changing the number of active sites available for wall reaction. We have assumed that this process can be approximated by a first-order reaction. According to Laidler (ref. 14), the rate constant  $k$  for such a reaction is given approximately by

$$k = \frac{a}{1 + bC_g} \quad (1)$$

where  $C_g$  is the gas-phase concentration of the adsorbed gas. This equation shows that  $k_{\text{Cl}}$  should decrease as the  $\text{CFCl}_3$  concentration increases. Equation (1) shows that  $k$  asymptotically approaches zero as  $C_g$  increases. However, we found a better match between experimental and theoretical results when  $k_{\text{Cl}}$  was allowed to decrease asymptotically, as in equation (1), but to a constant asymptote of 2.5 rather than zero.

This situation could occur if there were catalytic sites for Cl destruction that were not covered by  $\text{CFCl}_3$  adsorption. The equation for  $k$  could then be modified to

$$k = \frac{a}{1 + bC_g} + d \quad (1a)$$

where  $d$  is the rate constant appropriate for these uncovered sites.

The theory just presented requires that there be an excess of  $\text{CFCl}_3$  molecules present for wall adsorption. Our computations indicate that this is the situation. They show that only a small fraction of the  $\text{CFCl}_3$  is used up in any reaction. This is true even for 1- and 2-ppm of  $\text{CFCl}_3$ . For  $\text{Cl}_2$ -air mixtures, however, there is no excess  $\text{Cl}_2$ . Because  $\text{Cl}_2$  has a much higher photolysis rate constant than  $\text{CFCl}_3$ , it is always completely destroyed during the early part of any reaction. Thus, we would not expect any variation of  $k_{\text{Cl}}$  with initial  $\text{Cl}_2$  concentration for any of the low concentrations used in our work.

We can perform a simple computation to determine whether our values for  $k_{\text{Cl}}$  are at least plausible. Shuler and Laidler (ref. 15) give the following relation between a first-order surface reaction rate constant  $k$  and the recombination coefficient for the surface  $\gamma$ :

$$\gamma = \frac{4kV}{\bar{v}S} \quad (2)$$

where

- $\gamma$  ratio of number of molecules reacting per second at a surface to number of molecules hitting surface per second
- $V$  volume of reaction vessel
- $\bar{v}$  average molecular velocity
- $S$  surface area of reaction vessel

For the reaction chamber we used, this formula gives  $\gamma$  values ranging from  $1.8 \times 10^{-3}$  for  $k_{\text{Cl}} = 40 \text{ sec}^{-1}$  to  $9.1 \times 10^{-5}$  for  $k_{\text{Cl}} = 2 \text{ sec}^{-1}$ . These values are in the same range as those reported in reference 15 for a treated glass surface. Therefore, our  $k_{\text{Cl}}$  values are consistent with the theory of heterogeneous reactions given in reference 14.

## APPLICATION TO STRATOSPHERIC CONDITIONS

We have shown that  $\text{CFCl}_3$  permanently inhibits  $\text{O}_3$  formation in a laboratory experiment. As mentioned previously, the conditions in the chamber were different from those in the upper atmosphere. While our  $\text{O}_3$  concentrations were comparable to stratospheric levels, our  $\text{CFCl}_3$  concentrations were about  $10^5$  times higher than stratospheric levels (refs. 1 to 3). Moreover, our 3-hour irradiation time was about  $10^4$  times shorter than the estimated half-life of 2 to 4 years for  $\text{CFCl}_3$  in the stratosphere (ref. 16). The important chemical mechanism for  $\text{O}_3$  destruction should be the same for both conditions. However, the relative importance of various reactions may change with changing conditions. This possibility could cause the same chemical mechanism to give quite different trends for the effect of  $\text{CFCl}_3$  on  $\text{O}_3$  formation at stratospheric conditions. To check on this matter, we performed a few computations for a temperature of 220 K and a pressure of 0.0563 atmosphere. These conditions correspond to an altitude range of 20 to 30 kilometers. Figure 6 shows the results of two computations. The solid curve shows  $\text{O}_3$  formation in pure air at these altitude conditions. The value of  $J_7$  ( $\text{O}_2$  photolysis) used is  $1 \times 10^{-11} \text{ sec}^{-1}$  (ref. 17). Of course, all wall destruction reactions (for  $\text{O}_3$  and  $\text{Cl}$ ) are omitted in these computations. The dashed curve shows  $\text{O}_3$  formation in air containing 3 ppb of  $\text{CFCl}_3$ . It is clear that our chemical mechanism shows the same destructive effect of  $\text{CFCl}_3$  on  $\text{O}_3$  at altitude conditions as in our reaction chamber. And this is in the absence of all wall reactions. Under both sets of conditions,  $\text{O}_3$  concentration rises in the presence of  $\text{CFCl}_3$  but then peaks and falls to a lower value. It must be emphasized that these new computations in no way prove that  $\text{CFCl}_3$  in the stratosphere will significantly destroy  $\text{O}_3$ . There are many other effects in the stratosphere (diffusion, interactions with aerosols, etc.) that determine the steady-state  $\text{O}_3$  concentration. This computation simply demonstrates that the chemical model for our chamber experiment shows a similar destructive effect on  $\text{O}_3$  when used for stratospheric conditions.

## CONCLUDING REMARKS

In this work we have studied the effect of molecular chlorine ( $\text{Cl}_2$ ) and trichlorofluoromethane ( $\text{CFCl}_3$ ) in suppressing ozone ( $\text{O}_3$ ) production during the photolysis of air. One or 2 ppm of  $\text{Cl}_2$  temporarily delayed the formation of  $\text{O}_3$ . However, after about 200 minutes of reaction time the  $\text{O}_3$  concentration rose almost to the level that would be present in pure air. In the presence of 1 to 103 ppm of  $\text{CFCl}_3$ ,  $\text{O}_3$  concentration rose immediately, as it would in pure air. As  $\text{Cl}$  atoms were formed by the  $\text{CFCl}_3$  photolysis, the  $\text{O}_3$  formation was inhibited and either leveled off at a reduced steady-state value or else maximized and then decreased toward zero. The results are interpreted as a com-

combination of homogeneous gas-phase reaction and wall reaction effects. The difference in  $O_3$  behavior for the two systems can be explained by two factors. First, the initial concentration of  $CFCl_3$  was, in many cases, much larger than that of  $Cl_2$ . All the initial  $Cl_2$  was photolyzed, whereas only part of the  $CFCl_3$  was destroyed during a reaction. Thus, Cl atoms were continuously being formed during the entire reaction for  $CFCl_3$ . This was not true for the  $Cl_2$  reaction. Second, the effective wall reaction sink for Cl atoms was apparently greater in the  $Cl_2$  experiments than in the  $CFCl_3$  experiments. In any chamber experiment, the early part of the reaction will probably be controlled by gas-phase reaction. The last part will most likely be dominated by mixing and wall reaction effects caused by the accumulation of products at the walls. Therefore, the recovery of  $O_3$  formation in the  $Cl_2$ -air reaction was very likely due to the significant removal of Cl atoms from the gas phase. Otherwise, the final  $O_3$  concentration would be expected to decrease as the initial  $Cl_2$  concentration was increased. This idea is supported by our theoretical computations, which include a simulated first-order Cl wall removal reaction whose rate constant is high ( $40 \text{ sec}^{-1}$ ).

The  $CFCl_3$ -air system is much more complicated than the  $Cl_2$ -air system. The fact that our simple chemical mechanism predicts fairly well some of the  $O_3$  profiles does not necessarily mean that it is the correct mechanism. Our computations, using the idea of a variable rate of wall destruction of Cl atoms, agree semiquantitatively with the experimental results. However, more work must be done in order to add to our understanding of this photolysis reaction. Concentration profiles for species other than  $O_3$  are needed. Any valid chemical model for the complete reaction must agree with several concentration profiles, not just a single one. A more complete understanding of the  $ClO_x$  chemical system is necessary as one part of the global model of all processes occurring in the stratosphere.

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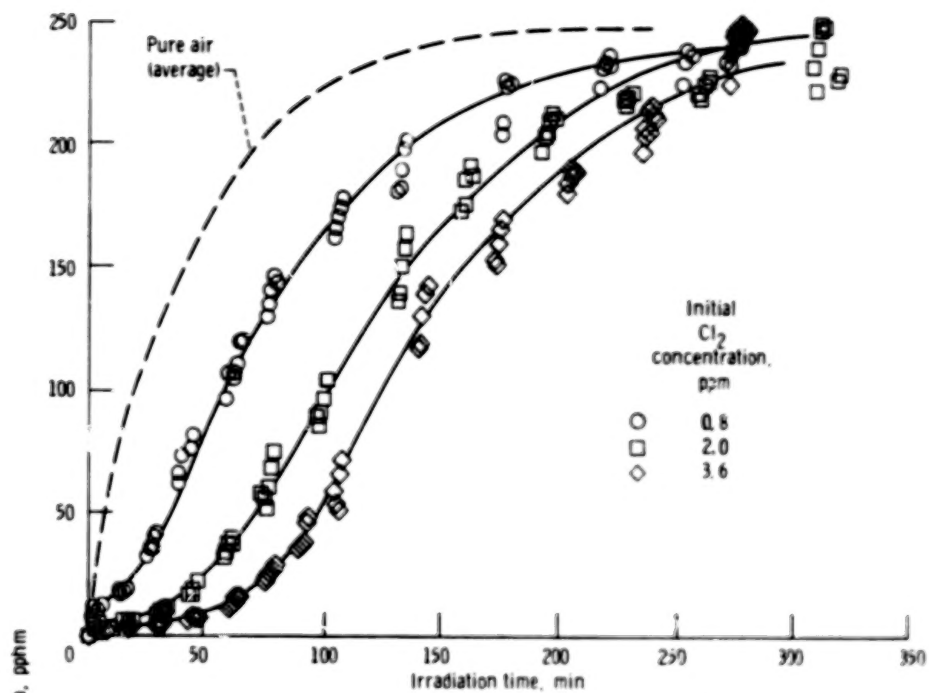
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TABLE I. - REACTIONS IN ClO<sub>x</sub> SYSTEM

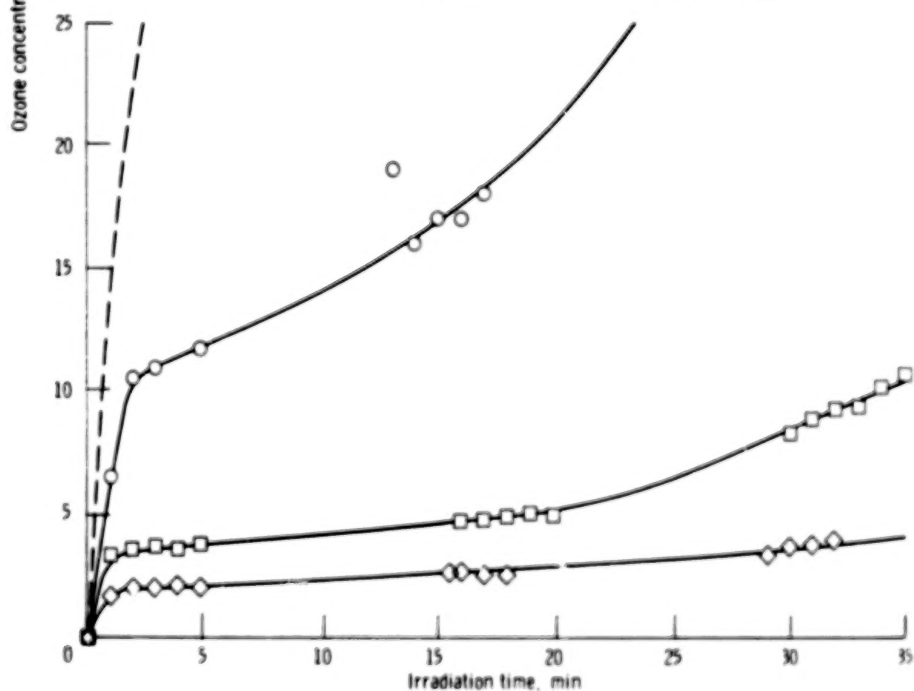
Number	Reaction	Coefficients in equation $k = AT^N \exp(-E_a/RT)$ (a)				Reference
		A	N	$E_a$		
				J/mole	cal/mole	
I	$Cl + O_3 \rightarrow ClO + O_2$	$1.3 \times 10^{13}$	0	1 423	340	18
II	$O + ClO \rightarrow Cl + O_2$	$3 \times 10^{13}$			0	19
III	$h\nu + Cl_2 \rightarrow 2Cl$	$5.9 \times 10^{-4}$			0	Adjusted from 20
IV	$2Cl + M \rightarrow Cl_2 + M$	$5.8 \times 10^{14}$		-6 694	-1600	20
V	$h\nu + ClO \rightarrow Cl + O$	$2 \times 10^{-3}$			0	20
VI	$O + Cl_2 \rightarrow ClO + Cl$	$5.6 \times 10^{12}$		12 970	3100	21
VII	$h\nu + O_2 \rightarrow O + O$	(b)				
VIII	$h\nu + O_3 \rightarrow O + O_2$	$3.55 \times 10^{-3}$			0	9
IX	$O + O_2 + M \rightarrow O_3 + M$	$3.8 \times 10^{13}$		-4 226	-1010	9
X	$O + O_3 \rightarrow O_2 + O_2$	$1.1 \times 10^{13}$		19 120	4570	9
XI	$ClO + ClO \rightarrow Cl + ClO_2$	$2.0 \times 10^{10}$			0	Adjusted from 22
XII	$Cl + ClO_2 \rightarrow Cl_2 + O_2$	$9.4 \times 10^{13}$			0	23
XIII	$ClO_2 + M \rightarrow Cl + O_2 + M$	$7.8 \times 10^{12}$		8 326	1930	20

<sup>a</sup> k has units of sec<sup>-1</sup> for photochemical reaction, cm<sup>3</sup> mole<sup>-1</sup> sec<sup>-1</sup> for bimolecular reaction, and cm<sup>6</sup> mole<sup>-2</sup> sec<sup>-1</sup> for termolecular reaction; R = 1.98717 cal mole<sup>-1</sup> K<sup>-1</sup>

<sup>b</sup> See text.



(a) Time-concentration profiles for irradiation time of 310 minutes.



(b) Expanded time-concentration profiles for first 35 minutes.

Figure 1. - Ozone formation in pure air and air containing various amounts of molecular chlorine ( $\text{Cl}_2$ ).

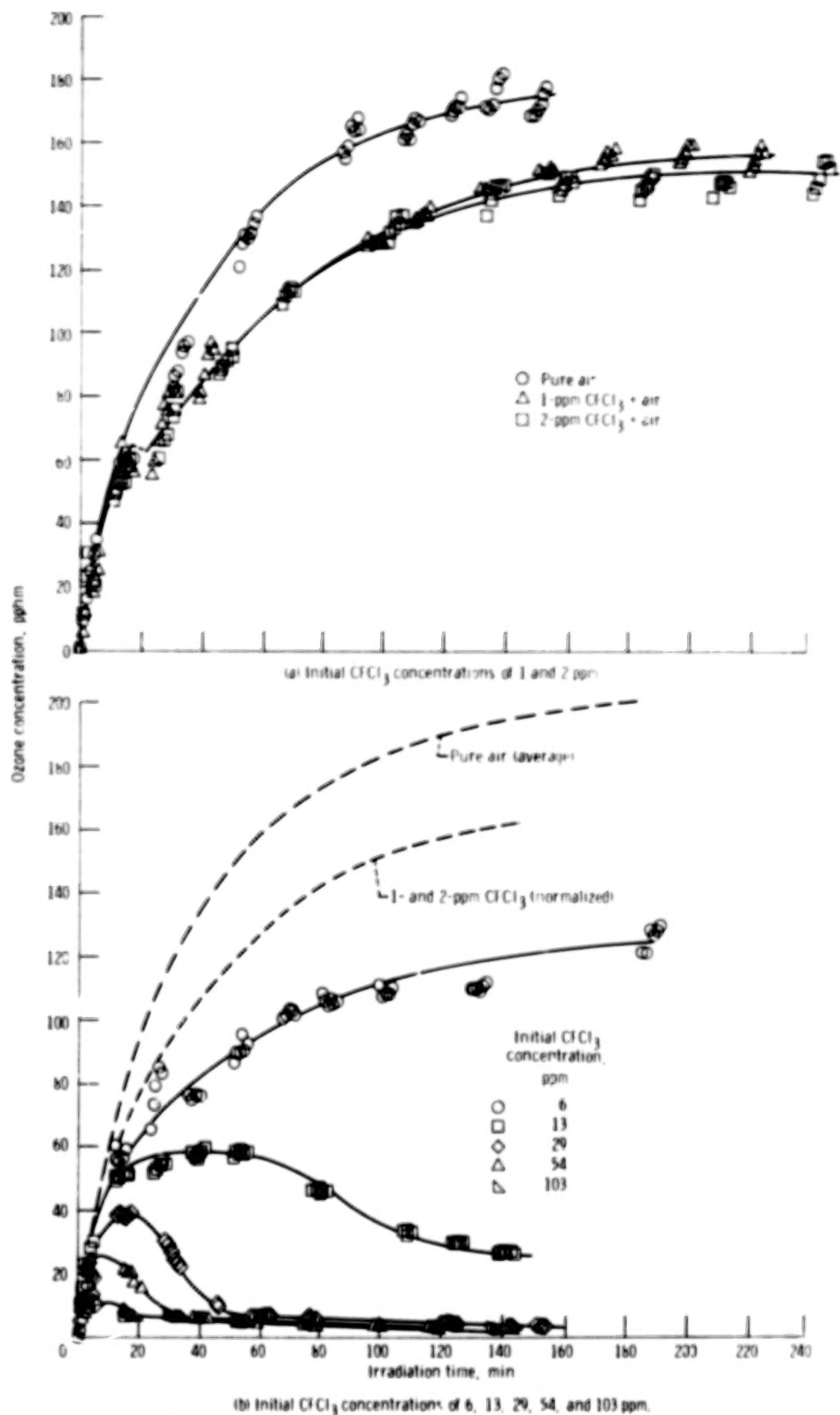


Figure 2 - Ozone formation in air and air containing various amounts of trichlorofluoromethane ( $\text{CFCl}_3$ ).

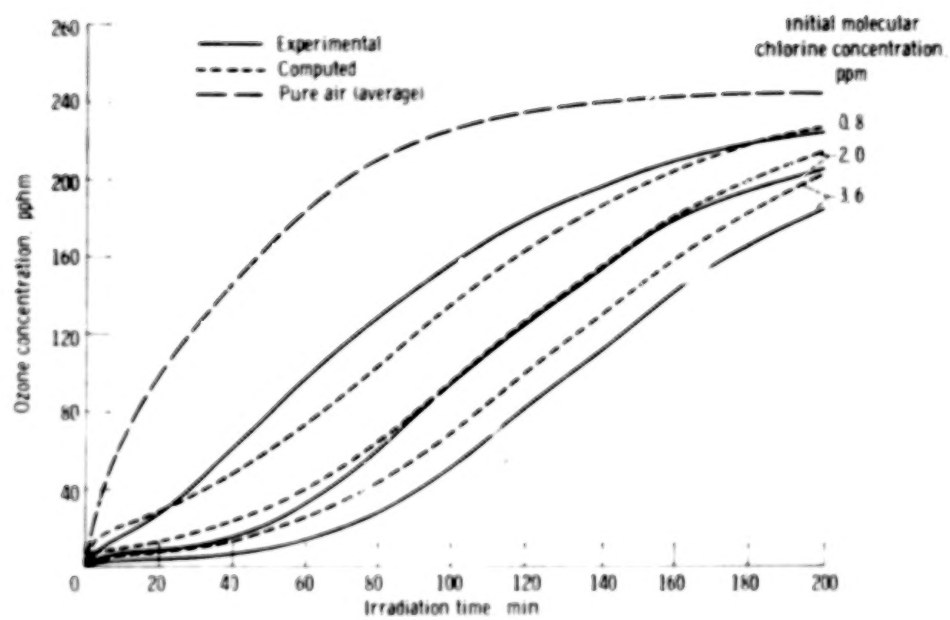


Figure 3 - Comparison of experimental and computed ozone formation in air and molecular chlorine mixtures

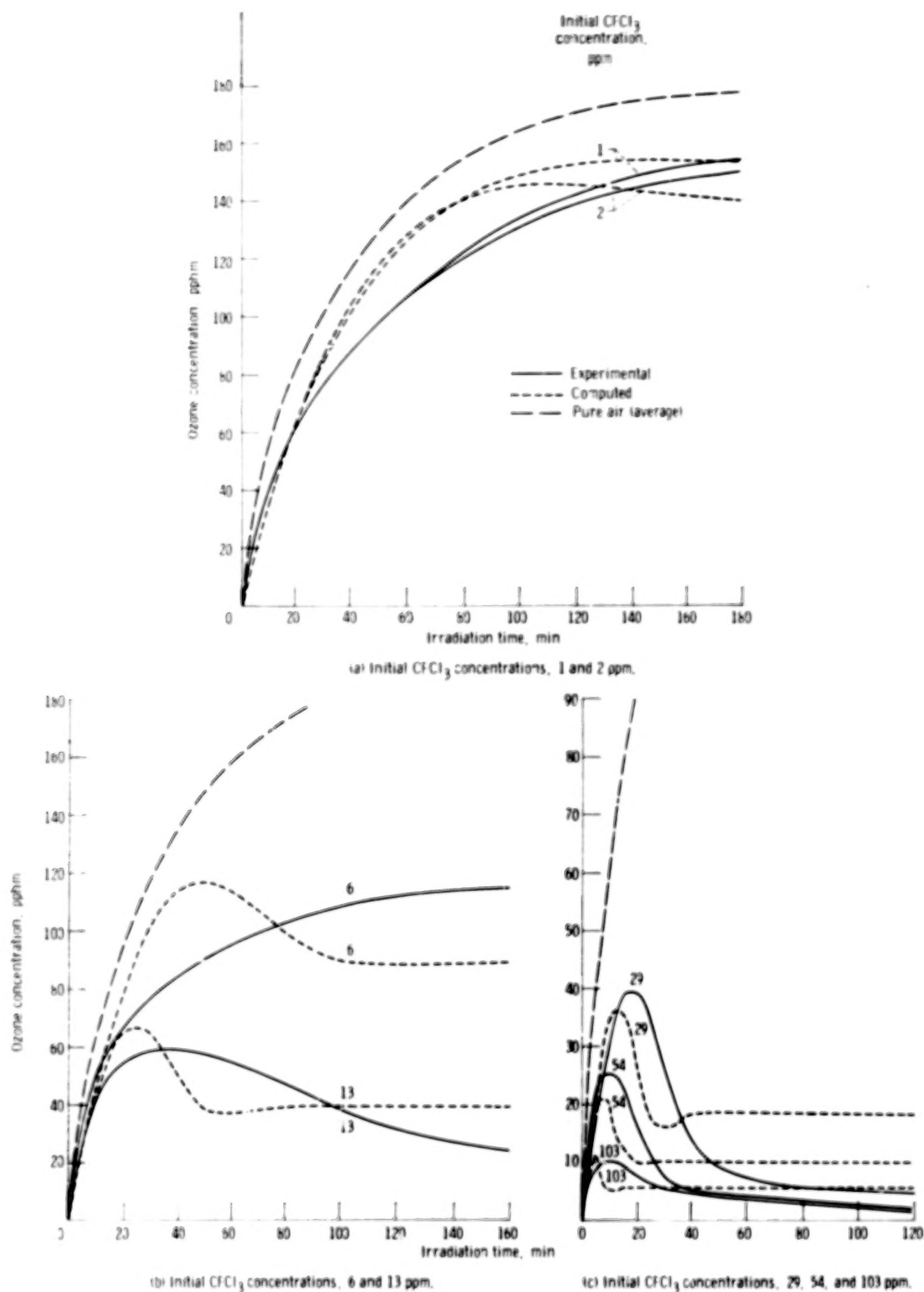


Figure 4 - Comparison of experimental and computed ozone formation in air and trichlorofluoromethane mixtures.



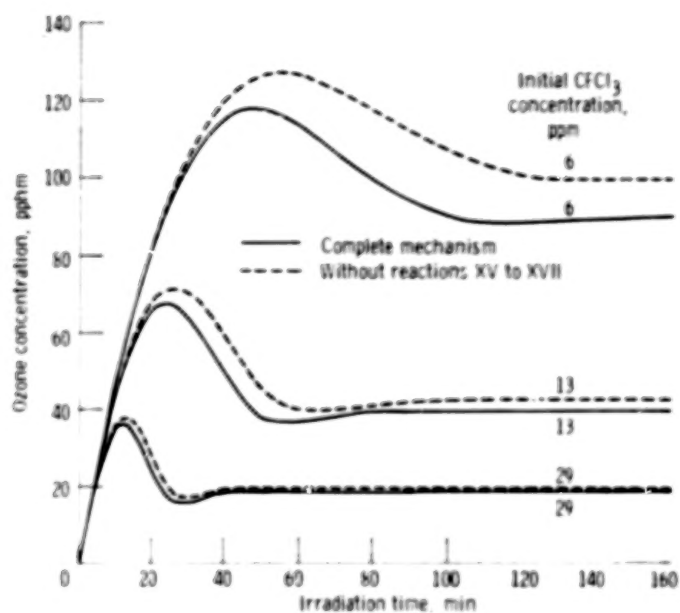


Figure 5 - Effect of trichlorofluoromethane photolysis mechanism on computed ozone profiles.

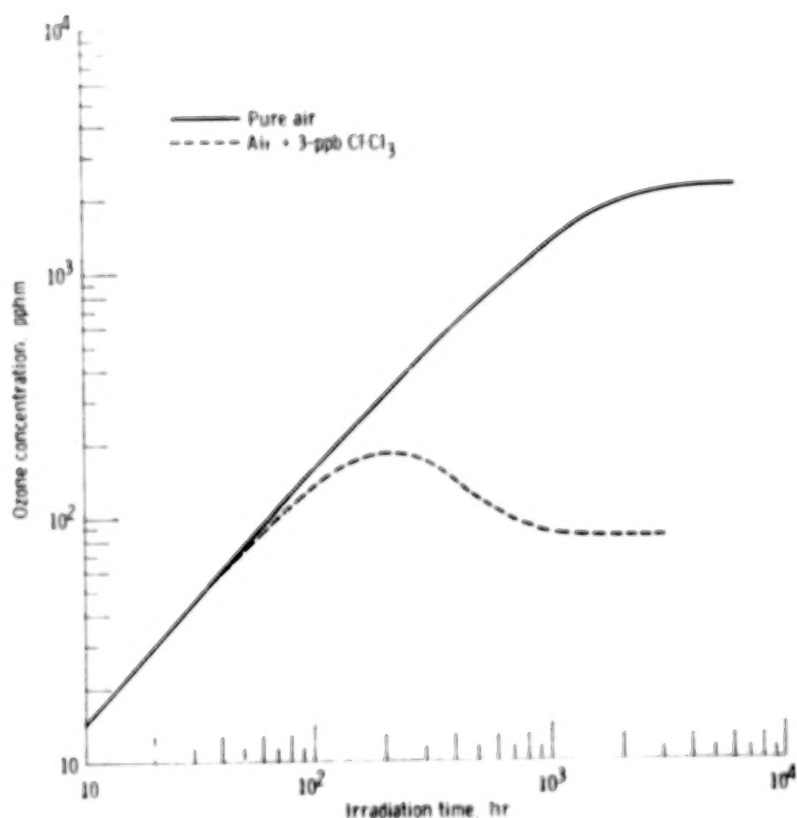


Figure 6 - Computed ozone formation at stratospheric altitude conditions: temperature, 220 K; pressure, 0.0363 atmosphere.

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16 Abstract  Mixtures of air with either $\text{Cl}_2$ or $\text{CFCl}_3$ were photolyzed in a reaction chamber by simulated solar radiation. Ozone formation was temporarily inhibited by $\text{Cl}_2$ and permanently inhibited by $\text{CFCl}_3$ . A chemical mechanism including gas-phase and wall reactions is proposed to explain these results. Wall destruction of Cl atoms is proposed; this reaction is more important for $\text{Cl}_2$ than for $\text{CFCl}_3$ . The $\text{CFCl}_3$ is assumed to be adsorbed on the chamber walls and to poison the sites for Cl destruction.			
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